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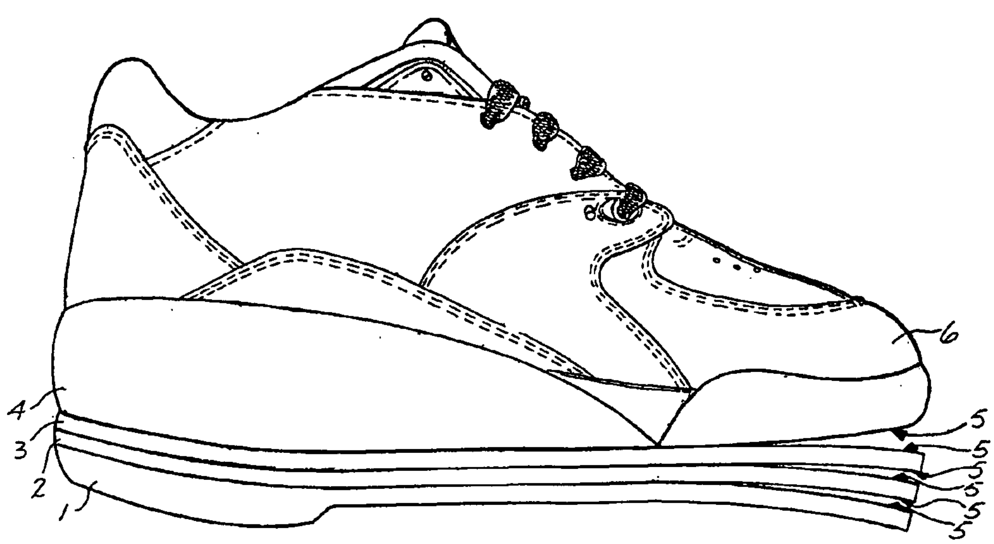


(57) Abstract

Methods for chemically modifying particular surfaces using plasma surface modification are provided. A method for preparing footwear having at least two components (1, 2, 3, 4) involves chemically modifying the surface of a component (5) using plasma surface modification. The modified component surface is then adhered to a surface of another component. Functionalities that are added to the component surface by this technique include chlorine, oxygen and amine functionalities. The adhesion of a substrate is enhanced by chemically modifying a surface of the substrate using plasma surface modification to include chlorine and oxygen-containing functionalities, chlorine and amine functionalities, or amine and oxygen functionalities.

METHODS FOR PLASMA MODIFICATION OF SUBSTRATES

Field of the Invention

The invention is directed to methods of plasma modification and to the use of plasma modification of plastics and monomers, such as used in the footwear industry.

Background of the Invention

Generally, popular footwear, such as sneakers and boots, have one or more components bonded together with an adhesive. Generally, at least one of the components is typically made of an elastomeric material. To enhance the adhesion between the component surfaces, the surfaces are cleaned using a solvent and then modified using a solvent-based or water-based primer. The primer modifies the surface of the component to contain additional or different chemical functionalities. These functionalities facilitate migration of the adhesive into the substrate, providing molecular mechanical locking and/or chemical bonding of the substrate with the adhesive.

Many of the commercially-useful primers are chlorinated primers, which are highly undesirable for environmental reasons. Additionally, it has been found that some primers make the surface more brittle, resulting in microcracks in the surface. Moreover, certain primers can discolor the surface, turning, for example, a white surface into a yellow surface. Another disadvantage of using a primer is that it is difficult to determine where and how much primer has been applied. Additionally, it has been found that primers can only provide a limited number of functionalities on the surface, namely, only up to about 8% based on the total number of atoms on the surface of the substrate, as determined by ESCA.

Thus, a need exists for an alternative method for modifying elastomeric surfaces and other surfaces used in the footwear industry that avoids the above-mentioned drawbacks.

Summary of the Invention

The present invention is directed to methods for modifying particular surfaces using plasma surface modification. In one embodiment, the invention is directed to a method for making footwear having at least two components. The surface of a component is chemically modified using plasma surface modification. The modified component surface is then adhered to another component composition. By this method, a substantially even distribution of functionalities are provided over the modified surface because of the ability of the plasma to penetrate cracks and small openings in the surface. Functionalities that are added to the component surface by this technique include, but are not limited to, chlorine, oxygen, carboxyl, hydroxyl, carbonyl, nitrogen and amine functionalities.

In another embodiment, the invention is directed to a method for enhancing the adhesion of a substrate. At least one surface of the substrate is modified using plasma surface

modification to include chlorine and oxygen-containing functionalities, chlorine and amine functionalities, or amine and oxygen-containing functionalities. The invention is also directed to a composition having at least one surface comprising chlorine and oxygen-containing functionalities, chlorine and amine functionalities, or amine and oxygen-containing functionalities bonded to its surface by plasma surface modification.

In another embodiment, the invention is directed to footwear having at least two components that are adhered to each other. The adhered surface of at least one component contains functionalities chemically bonded to it by plasma surface modification.

Description of the Drawings

These and other features and advantages of the present invention will be better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings wherein:

FIG. 1 is an illustration of a shoe according to the invention.

FIG. 2 is a schematic depiction of plasma modification equipment useful for the methods of the invention.

Detailed Description of the Invention

The present invention is directed to methods for modifying particular surfaces using plasma surface modification. The term "plasma" refers to an ionized gas containing positive and negative charges, free radicals and electrons. The term "plasma surface modification" generally refers to the process of affecting chemical changes in a substrate surface by exposing it to low pressure and/or low temperature plasma.

It has been found that the plasma treatment of the invention provides excellent wettability of the polymeric surface with various adhesives, such as epoxies, urethanes and hot melts. To obtain improved adhesion, it is desirable to increase the wettability of the surface, i.e., the extent of direct and continuous contact between the adhesive and the surface(s) being bonded. Wettability is essential for reactive adhesives such as contact (pressure-sensitive adhesives) and hot melt adhesives. Non-reactive adhesive systems rely predominantly on several adhesion mechanisms, including mechanical interlocking, molecular diffusion and electrostatic interactions between the adhesive and polymer surface.

Another key feature for optimum adhesion, particularly for reactive adhesives such as epoxy and isocyanate cure systems, is the adhesive's ability to chemically bond to the substrate. Thus, the substrate must have the correct chemistry to chemically react with the adhesive. For example, for an amine cured epoxy system, the epoxy portion of the system chemically reacts with the amine forming a covalent bond between the carbon formerly bonded to the epoxide oxygen and the nitrogen of the amine. The reaction forms a strong three-dimensional molecular structure providing excellent cohesive strength. If amine

functionalities are present on the surface of the substrates to be bonded with an amine cured epoxy, the resulting product of the chemical reaction of the adhesive and substrate will include the amine functionalities on the surface, which will be incorporated into the molecular network of the adhesive. This molecular network enhances the adhesion between the substrate and the adhesive. The present invention provides methods for enhancing the ability of substrates to adhere to other compositions, particularly to adhesives.

Particularly suitable substrates that can be modified in accordance with the invention include elastomeric substrates, thermoplastic substrates, and thermoset plastics. Nonlimiting examples of elastomeric substrates include styrene-butyl-styrene rubber (SBS), styrene butyl rubber (SBR), polyvinylchloride (PVC), ethylene vinyl acetate (EVA), polyurethane rubber (PU), polybutadiene rubber (BR), chlorobutyl rubber (CLLR), synthetic polyisoprene rubber (IR), neoprene rubber (CR), ethylene propylene rubber (EPDM), silicone elastomer, nitrile rubber (NBR), polyacrylic rubber (ACM), fluoroelastomers, polyolefin thermoplastic elastomers, polyolefin thermoset elastomers, such as Engage™ commercially available from DuPont Dow, and halogenated polyolefin thermoplastic elastomers. Nonlimiting examples of thermoplastic substrates include polyolefins, fluoropolymers, polystyrene and styrene copolymers, polyvinylchlorides, polyvinylacetates, acrylic thermoplastics, aliphatic polyethers, polyesters, polyurethanes, silicones, polydienes, phenolic polymers, polycarbonates, polyamides, poly(ethylene terephthalate), polyformaldehydes, poly(methyl methacrylate), and acrylonitrile-butadiene-styrene copolymers. Suitable thermoset plastics include, but are limited to, epoxies, polyurethanes, and cyanoacrylates. Other substrates frequently used in the footwear industry can also be modified by the methods of the invention, such as nylon, Kevlar, and imitation and natural leather.

As used herein, the term "footwear" includes, but is not limited to, shoes, sneakers, boots, sandals, and slippers. FIG. 1 illustrates a shoe according to the invention having multiple components, namely an out sole **1**, mid soles **2, 3** and **4**, and an upper **6**, each having surfaces **5**. Typically, the out sole **1** is made of a durable rubber material. The mid soles **2**, **3** and **4** are typically made of a foam material. The upper **6** can be made of any suitable material such as nylon, canvas, leather and other naturally-occurring and synthetic polymers. Any of the component surfaces **5** can be modified in accordance with the invention. The components can then be adhered to one another, either directly or using an adhesive. When the components are adhered to one another, they can be in any suitable form, including both solid and liquid forms. For example, the out sole could be composed of a solid polyurethane and the mid sole composed of a solid foam, in which case one or both components could be modified and an adhesive would be used to adhere the components. Alternatively, the out sole could be composed of a solid polyurethane and the mid sole composed of a liquid material that is capable of curing into a foam, in which case the out sole is modified and the mid sole is formed onto the out sole by pouring the liquid preformed material onto the out

sole and subsequently curing the liquid material. In this latter embodiment, the resulting construction comprises a substantially solid foam mid sole adhered to the out sole. A third possibility would involve a liquid composition cured onto a solid plasma treated mid sole adhered to form an out sole.

The plasma-modified substrates can be bonded using a wide variety of adhesives. Suitable adhesives include, but are not limited to, isocyanate-type polyurethane hot melt, isocyanate-type water base polyurethane, silicone-based, polysulfide, cyanoacrylate, epoxy, polyurethane, polyamide, polyimide, polyamide-imide, polyamide-epichlorohydrin, acrylic, polyester, butadiene-acrylonitrile, butadiene-styrene, neoprene, butyl rubber, polyisobutylene, latex, ethylenevinylacetate, epoxy-nitrile, phenolic nitrile-phenolic, resorcinol, and polyvinyl adhesives.

The methods of the invention can be carried out using any known type of plasma surface modification equipment, such as the apparatus depicted in FIG. 2. The apparatus comprises a reactor vessel **10** having a reaction chamber **11** into which is placed a substrate **12** to be modified. If desired, one or more shelves **13** can be provided within the reaction chamber **11** for placement of one or more substrates **12** within the chamber. Preferably the reaction chamber **11** is made of metal, such as aluminum, but can also be made of other suitable materials such as quartz. The reaction vessel **10** can be designed for batch operation or for continuous operation as desired. Preferably, the reaction chamber **11** is capable of being substantially evacuated, i.e., to a pressure within the range of about 10^{-3} to about 700 Torr, preferably about 10^{-2} to about 0.5 Torr.

One or more gas sources **14** are provided, from which one or more gases flow into the reaction chamber **11** through mass flow controllers **16**. If desired, different gases from different gas sources **14** can be mixed in a mixer **15** prior to introduction to the reaction chamber **11**. In addition, different gases or combinations of gases can be introduced into the plasma reactor at different times during the processing or treatment.

Located within the reaction chamber **11** is an electrode **18**. In the illustrated embodiment, the electrode **18** is a barrel-type electrode having a generally cylindrical shape. If desired, the shelves **13** can be electrified in place of or in addition to the barrel-type electrode **18**. The electrode **18** acts as a cathode and is connected to a variable frequency power source **22**. The reactor vessel **10**, which is electrically isolated from the electrode **18**, acts as an anode and is grounded. Any other suitable electrode configuration could also be used.

If desired, the electrode can include magnetic confinement. An example of such an electrode is described in U.S. Patent No. 5,433,786, the disclosure of which is incorporated herein by reference.

The variable frequency power source **22** furnishes the electrical power necessary to generate the plasma. If desired, the plasma power can be turned on and off rapidly or

"pulsed" during the processing or treatment. For the applications of the present invention. the power source **22** should be capable of generating alternating current electrical power in the range of 50 to 5000 watts with a frequency of 1000 Hz to 5 GHz, and preferably generates radio frequency energy, low frequency energy or microwave frequency energy. Examples of suitable power sources **22** for use in the present invention arc 13.56 MHz power generators and 40 KHz power generators.

In operation, the reaction chamber **11** is first evacuated by means of a vacuum pump **24**. Any suitable vacuum pump **24** can be used, preferably a pump that can accommodate an ultimate vacuum of 5 millitorr. A suitable vacuum pump **24** for use with the present invention is sold under the trade designation 2033C by Alcatel International (Hingham, Massachusetts).

One or more gases are then introduced into the reaction chamber **11** at a predetermined flow rate, preferably from about 50 to 1000 sccm (standard cubic centimeters per minute), more preferably from about 50 to about 250 sccm, and still more preferably from about 80 to about 125 sccm, through supply line **26**. The flowrate of the gases is adjusted to achieve a predetermined pressure, prcferably from about 0.020 to about 1.000 torr, more preferably from about 0.100 to about 0.500 torr, even more preferably from about 0.080 to about 0.500 torr, still more preferably from about 0.140 to about 0.250 torr, and yet more preferably from about 0.170 to about 0.200 torr. When the desired pressure is achieved, the variable frequency power source **22** is turned on to generate an electric field under preselected frequency and power conditions to ionize the gases, thereby forming a plasma. Methods of generating an electric field between electrodes are well-known in the art. The electric field is maintained for a predetermine time period, preferably from about 15 seconds to about 90 minutes, more preferably 30 seconds to about 30 minutes, still more preferably from about 2 to about 12 minutes, and yet more preferably from about 8 to about 12 minutes, so that the substrate is explosed to the plasma for that time period.

The plasma creates a high density of free radicals, ions and electrons, both in the gas phase and on the surface of the substrate. The surface free radicals are created by direct attack of the gas-phase free radicals, ions, electrons and/or by photodecomposition of the surface by vacuum-ultraviolet light generated by the plasma. The surface free radicals are then able to react either with each other or with free radicals in the plasma environment. When the surface free radicals react with free radicals in the plasma environment, functional groups are formed on the surface of the substrate. The modification generally affects only the top few molecular layers of the substrate (approximately 50 to 100 Å), and thus the bulk properties of the substrate are not altered. This surface modification technique enhances the chemical reactivity of the surface of the substrate.

The gases used in the inventive methods depend on the particular application, namely the substrate and adhesive to be used. As explained above, the substrate should be modified

to contain functionalities that enhance the wettability of the adhesive to the substrate. For example, if an epoxy adhesive is used, amine functionalities are preferred. Alternatively, if a hot melt adhesive, such as a moisture-cured (isocyanate) hot melt, is used, preferably the substrate surface is modified to include chlorine or oxygen functionalities, and more preferably to contain both chlorine and oxygen functionalities.

If chlorine functionalities are desired, the plasma can comprise carbon tetrachloride, chloroform or any other organic volatile material that contains chlorine. If oxygen functionalities are desired, the plasma can contain any volatile compound containing oxygen, for example, nitrous oxide, carbon dioxide, oxygen or air. If the substrate already contains oxygen functionalities, it may be further modified to a lower oxidation state, such as from a carbonyl functionality to a hydroxyl functionality, using hydrogen gas. If amine functionalities are desired, the plasma can contain any organic volatile composition that contains nitrogen, such as ammonia or nitrogen. Other functionalities could also be added to the substrate surface in accordance with the invention.

The lifetime of the chemical functionalities on substrate surfaces are typically short, ranging from only a few minutes to several days, resulting in a decrease of functionalities at the top molecular level of the surface. One approach to address this problem is to increase the amount of functionalities on the surface. However, it is undesirable to include too large a number of functionalities (e.g., overoxidation) because it tends to reduce the molecular length of the polymer chains on the substrate surface, forming loose boundary layers on the surface. With respect to chlorine functionalities, preferably the surface is modified to contain from about 0.5% to about 25%, more preferably from about 5% to about 20%, still more preferably from about 15% to about 20%, chlorine functionalities. With respect to oxygen functionalities (including carboxyl groups, hydroxyl groups and carbonyl groups), preferably the surface is modified to contain from about 1% to about 30%, more preferably from about 2% to about 20%, still more preferably from about 5% to about 15%, and yet more preferably from about 10% to about 15%, oxygen functionalities. With respect to amine functionalities, preferably the surface is modified to contain from about 0.1% to about 30%, more preferably 0.5% to about 20%, even more preferably from about 2% to about 10%, and still more preferably from about 8% to about 10%, amine functionalities. In a particularly preferred embodiment, the substrate is modified to contain from about 4% to about 15%, more preferably from about 12% to about 15%, chlorine functionalities and from about 5% to about 15%, more preferably from about 7% to about 9%, oxygen functionalities. In another preferred embodiment, the substrate is modified to contain from about 5% to about 15%, more preferably from about 12% to about 15%, chlorine functionalities and from about 3% to about 10% amine functionalities. In yet another preferred embodiment, the substrate is modified to contain from about 3% to about 10% amine functionalities and from about 5% to about 15%, more preferably from about 7% to about 9%, oxygen functionalities. The identified

percentages of functionalities are atom percentages, excluding hydrogen, as determined by electron spectroscopy for chemical analysis (ESCA). Another approach to increase the lifetime of the functionalities is by crosslinking the substrate by including one or more inert gases, such as helium and argon, in the plasma, as described in Schonhorn, H. et al. 1967 J. App. Polym. Sci. 11, p. 1461, and Schonhorn, H. et al., 1966 J. Polym. Sci. B4, p. 203, the disclosures of which are incorporated herein by reference.

The gases for use in the present invention can be vaporized from liquid form if necessary prior to entry into the reactor chamber. Preferably, the liquid outside of the chamber is heated isothermally such that sufficient vapor is supplied constantly to the chamber. Alternatively, an inert carrier gas such as helium or argon can be transported through the liquid to obtain a diluted vapor mixture of desired composition.

Gaseous reactants, such as oxygen, are suitable for reaction in plasma, alone or with an inert carrier gas to insure proper metering into the reaction chamber. Gaseous reactants may be supplied from an external source through a series of inlet pipes into the reactor chamber. The technical particulars of channeling various gases into a reactor chamber are well known in the art. For example, each gas conduit may be connected to a central feed line that carries the gases into the reaction chamber. If desired, the gaseous reactants can be mixed with a carrier gas such as argon to improve their flow into the reaction chamber. In some cases, a carrier gas has been found to improve the uniformity of plasma density and gas pressure within the reaction chamber. The carrier gas may be premixed with the gaseous reactants or may be fed into the supply line by a separate inlet. The flow of carrier and reactant gases into the reaction chamber may be governed by mass flow controller valves, which are well known in the art, and which serve to both measure and control the flow of gases.

After passing over the substrate surface, any gases that have not reacted with the surface may be directed out of the reaction chamber through an exit valve and then to a gas pumping and exhaust system (not shown). Means for expelling these excess materials from the reaction chamber are well-known in the art.

Prior to modification, the substrate surface may be cleaned by washing with water or an organic solvent, such as isopropanol, acetone, methanol, or the like. This washing step removes dirt, contaminants, and additives such as wetting agents from the surface. However, in some cases it has been found that the plasma treatment may achieve the required cleaning.

EXAMPLES

Examples 1 to 16

In Examples 1 to 16, the surfaces of several substrates, styrene-butyl-styrene rubber (SBS), ethylene vinyl acetate (EVA), Engage™ (ENG), styrene butyl rubber (SBR), polyvinylchloride (PVC), synthetic leather (SLR), and natural leather (NLR), were modified

by plasma surface modification. The plasma process conditions are indicated, where time indicates the amount of time that power was provided by the power source to generate an electric field. The plasma contained gases as indicated, which were provided at a flow rate sufficient to achieve the indicated pressure.

Within 12 hours of the plasma treatment, the modified substrates were bonded together or to canvas, as indicated, using a hot melt moisture cure adhesive system sold under the name Rapidex™ (H.B. Fuller Co., St. Paul, Minnesota). During adhesive cooling, 45 psi of pressure were applied to the bonded samples. Mechanical testing was conducted on the samples approximately 72 to 120 hours after bonding. Namely, a Tee Peel tension pull test was conducted on each sample pursuant to ASTM D412-97. The pull rate was 4 inches per minute. Using this test, preferably the bonded samples are able to withstand at least about 14 ppi (about 6.3 Kg/in^2), and more preferably at least about 35 ppi (about 15.9 Kg/in^2).

Table 1 describes the plasma process conditions and the mechanical tests results for each sample.

TABLE 1

Example	Materials Bonded	Plasma Process Conditions Time	Power	Pressure	Gases	Test Results
1	SBS/EVA	5 min.	400 watts	0.200 torr	$N_2O/CHCl_3$	19.9 Kg/in^2
2	SBS/EVA	10 min.	400 watts	0.200 torr	$N_2O/CHCl_3$	31.0 Kg/in^2
3	SBS/EVA	20 min.	400 watts	0.200 torr	$N_2O/CHCl_3$	20.5 Kg/in^2
4	SBS/EVA	10 min.	700 watts	0.200 torr	$N_2O/CHCl_3$	22.4 Kg/in^2
5	SBS/SBS	10 min.	400 watts	0.250 torr	N_2O	11.4 Kg/in^2
6	EVA/EVA	10 min.	400 watts	0.250 torr	N_2O	10.9 Kg/in^2
7	SBS/ENG	20 min.	400 watts	0.180 torr	$He/CHCl_3$	17.7 Kg/in^2
8	SBS/ENG	20 min.	400 watts	0.200 torr	$He/CHCl_3$	15.8 Kg/in^2
9	SBS/SBS	5 min.	400 watts	0.180 torr	$N_2O/CHCl_3$	20.5 Kg/in^2
10	SBS/SBS	10 min.	400 watts	0.180 torr	$N_2O/CHCl_3$	45.8 Kg/in^2
11	SBS/SBS	10 min.	400 watts	0.200 torr	$air/CHCl_3$	24.6 Kg/in^2
12	SBS/canvas	10 min.	700 watts	0.200 torr	$O_2/CHCl_3$	28.5 Kg/in^2
13	SBR/canvas	10 min.	700 watts	0.200 torr	$O_2/CHCl_3$	20.6 Kg/in^2
14	PVC/canvas	10 min.	700 watts	0.200 torr	$O_2/CHCl_3$	19.9 Kg/in^2
15	SLR/canvas	10 min.	700 watts	0.200 torr	$O_2/CHCl_3$	7.6 Kg/in^2
16	NLR/canvas	10 min.	700 watts	0.200 torr	$O_2/CHCl_3$	22.5 Kg/in^2

Example 17

The surfaces of two SBS substrates are modified by plasma surface modification. The plasma contains chloroform ($CHCl_3$) and is provided at a flow rate sufficient to achieve a pressure of 0.125 torr. 700 watts are provided to generate an electric field for 10 minutes. Within 12 hours of the plasma treatment, the modified surfaces of the substrates are bonded together using a hot melt moisture cure adhesive system sold under the name Rapidex™.

The above descriptions of exemplary embodiments of footwear, modified substrates and methods for modifying substrates using plasma surface modification are for illustrative purposes. Because of variations which will be apparent to those skilled in the art, the present invention is not intended to be limited to the particular embodiments described above. The scope of the invention is defined in the following claims. Further, it should be understood that the methods of the invention can function in accordance with the practice of the invention in the absence of any elements or materials not specifically described herein as being part of the methods.

I claim:

1. A method for preparing footwear having at least two components, the method comprising:

chemically modifying the surface of a component using plasma surface modification; and

adhering the modified component surfacc to a another component composition to form a multi-component construction.

2. A method according to claim 1, wherein a solid component surface is adhered to another solid component surface.

3. A method according to claim 1, wherein a liquid material is adhered to a solid component surface to form a multi-component construction.

4. A method according to claim 1, wherein at least one component comprises a composition selected from the group consisting of elastomeric compositions, thermoplastic compositions, thermoset plastics, and leather.

5. A method according to claim 1, wherein at least one component comprises a composition selected from the group consisting of styrene-butyl-styrene rubbers, styrene butyl rubbers, polyvinylchlorides, ethylene vinyl acetate, polyurethanes, polybutadienes, chlorobutyl rubbers, synthetic polyisoprene rubbers, neoprenes, ethylene propylene rubbers, silicone elastomers, nitrile rubbers, polyacrylic rubbers, fluoroelastomers, polyolefin thermoplastic elastomers, halogenated polyolefin thermoplastic elastomers, and thermoplastic polymers thereof.

6. A method according to claim 1, wherein at least one component comprises a composition selected from the group consisting of polyolefins, fluoropolymers, polystyrene and styrene copolymers, polyvinylchlorides, polyvinylacetates, acrylic thermoplastics, aliphatic polyethers, polyesters, polyurethanes, silicones, polydienes, phenolic polymers, polycarbonates, polyamides, poly(ethylene terephthalate), polyformaldehydes, poly(methyl methacrylate), acrylonitrile-butadiene-styrene copolymers, epoxies, and cyanoacrylates.

7. A method according to claim 1, wherein the component surface is adhered to another component surface using an adhesive.

8. A method according to claim 7, wherein the adhesive is selected from the group consisting of isocyanate-type polyester hot melt, isocyanate-type water base polyurethane, silicone-based, polysulfide, cyanoacrylate, epoxy, polyurethane, polyamide, polyimide, polyamide-imide, polyamide-epichlorohydrin, acrylic, polyester, butadiene-acrylonitrile, butadiene-styrene, neoprene, butyl rubber, polyisobutylene, latex. ethylenevinylacetate, epoxy-nitrile, phenolic nitrile-phenolic, resorcinol, and polyvinyl adhesives.

9. A method according to claim 7, wherein the adhesive is selected from the group consisting of isocyanate-type polyester hot melt, isocyanate-type water base polyurethane, and silicone-based adhesives.

10. A method according to claim 1, wherein the surface is modified to contain chlorine functionalities.

11. A method according to claim 1, wherein the surface is modified to contain oxygen functionalities.

12. A method according to claim 1, wherein the surface is modified to contain oxygen and chlorine functionalities.

13. A method according to claim 1, wherein the surface is modified to contain amine functionalities.

14. A method according to claim 1, wherein the surface contains oxygen functionalities and is modified with hydrogen-containing plasma to reduce one or more of the oxygen functionalities.

15. A method according to claim 1, wherein two component surfaces are modified using plasma surface modification and those two component surfaces are adhered to one another.

16. A method for enhancing the adhesion of a substrate, comprising modifying at least one surface of the substrate using plasma surface modification to include both chlorine and oxygen-containing functionalities.

17. A method according to claim 16, wherein the surface is modified to contain from about 4 atom % to about 15 atom % chlorine functionalities and from about 5 atom % to about 15 atom % oxygen functionalities.

18. A method according to claim 17, wherein the surface is modified to contain from about 12 atom % to about 15 atom % chlorine functionalities.

19. A method according to claim 17, wherein the surface is modified to contain from about 7 atom % to about 9 atom % oxygen functionalities.

20. A method according to claim 19, wherein the surface is modified to contain from about 12 atom % to about 15 atom % chlorine functionalities.

21. A method according to claim 16, wherein the substrate comprises at least one composition selected from the group consisting of elastomeric substrates, thermoplastic substrates, and thermoset plastics.

22. A method according to claim 16, wherein the substrate is exposed to plasma for a time of about 2 to about 12 minutes.

23. A method according to claim 16, wherein the substrate surface is modified at a pressure of from about 0.100 to about 0.500 torr.

24. A method according to claim 16, wherein the substrate surface is modified at a pressure of from about 0.140 to about 0.250 torr.

25. A method according to claim 16, wherein the substrate surface is modified at a pressure of from about 0.170 to about 0.200 torr.

26. A method according to claim 16, wherein the substrate is exposed to radio frequency energy.

27. A method according to claim 16, wherein the substrate is exposed to low frequency energy.

28. A method according to claim 16, wherein the substrate is exposed to microwave frequency energy.

29. A method for enhancing the adhesion of a substrate, comprising modifying at least one surface of the substrate using plasma surface modification to include both chlorine and amine functionalities.

30. A method according to claim 29, wherein the surface is modified to contain from about 5 atom % to about 15 atom % chlorine functionalities and from about 3 atom % to about 10 atom % amine functionalities.

31. A method for enhancing the adhesion of a substrate, comprising modifying at least one surface of the substrate using plasma surface modification to include both amine and oxygen-containing functionalities.

32. A method according to claim 31, wherein the surface is modified to contain from about 3 atom % to about 10 atom % amine functionalities and from about 5 atom % to about 15 atom % oxygen functionalities.

33. A composition comprising at least one surface having improved adhesion, the surface comprising chlorine and oxygen-containing functionalities bonded to its surface by plasma surface modification.

34. A composition according to claim 33, wherein the surface contains from about 4 atom % to about 15 atom % chlorine functionalities and from about 5 atom % to about 15 atom % oxygen functionalities.

35. A composition according to claim 33, wherein the surface contains from about 12 atom % to about 15 atom % chlorine functionalities and from about 7 atom % to about 9 atom % oxygen functionalities.

36. A composition according to claim 33 comprising at least one composition selected from the group consisting of elastomeric substrates, thermoplastic substrates, and thermoset plastics.

37. A composition comprising at least one surface having improved adhesion, the surface comprising chlorine and amine functionalities bonded to its surface by plasma surface modification.

38. A composition according to claim 37, wherein the surface contains from about 4 atom % to about 15 atom % chlorine functionalities and from about 3 atom % to about 10 atom % amine functionalities.

39. A composition comprising at least one surface having improved adhesion, the surface comprising amine and oxygen-containing functionalities bonded to its surface by plasma surface modification.

40. A composition according to claim 39, wherein the surface contains from about 3 atom % to about 10 atom % amine functionalities and from about 5 atom % to about 15 atom % oxygen functionalities.

41. Footwear having at least two components that are adhered to each other, wherein the adhered surface of at least one component contains functionalities chemically bonded to it by plasma surface modification.

42. Footwear according to claim 41, wherein the at least one component surface containing functionalities is made of a composition selected from the group consisting of elastomeric substrates, thermoplastic substrates, and thermoset plastics.

43. Footwear according to claim 41, wherein the at least two components are adhered to one another using an adhesive.

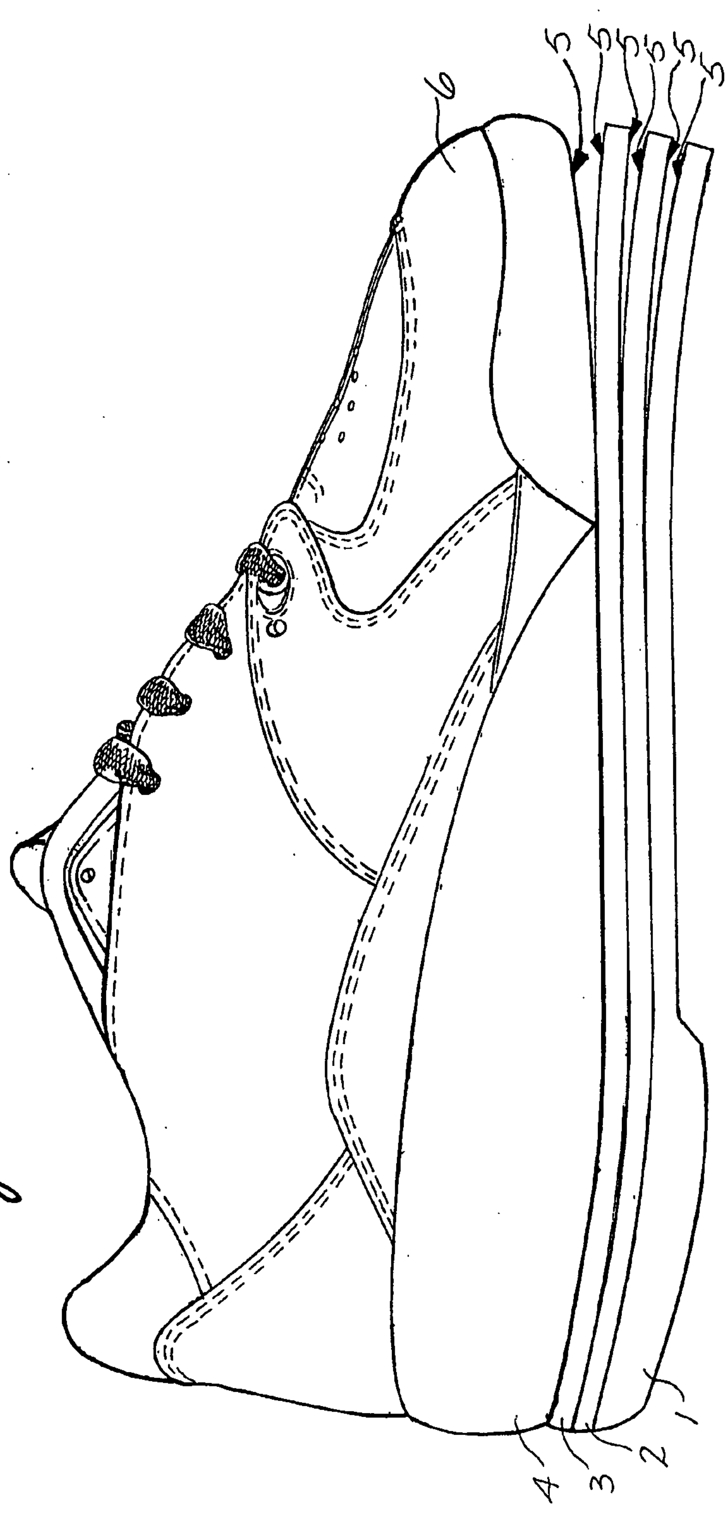
44. Footwear according to claim 41, wherein the at least one component surface is modified to contain chlorine functionalities.

45. Footwear according to claim 41, wherein the at least one surface is modified to contain oxygen functionalities.

46. Footwear according to claim 41, wherein the at least one surface is modified to contain oxygen and chlorine functionalities.

47. Footwear according to claim 41, wherein at least two component surfaces contain functionalities chemically bonded to them by plasma surface modification and those two component surfaces are adhered to one another.

Fig. 1



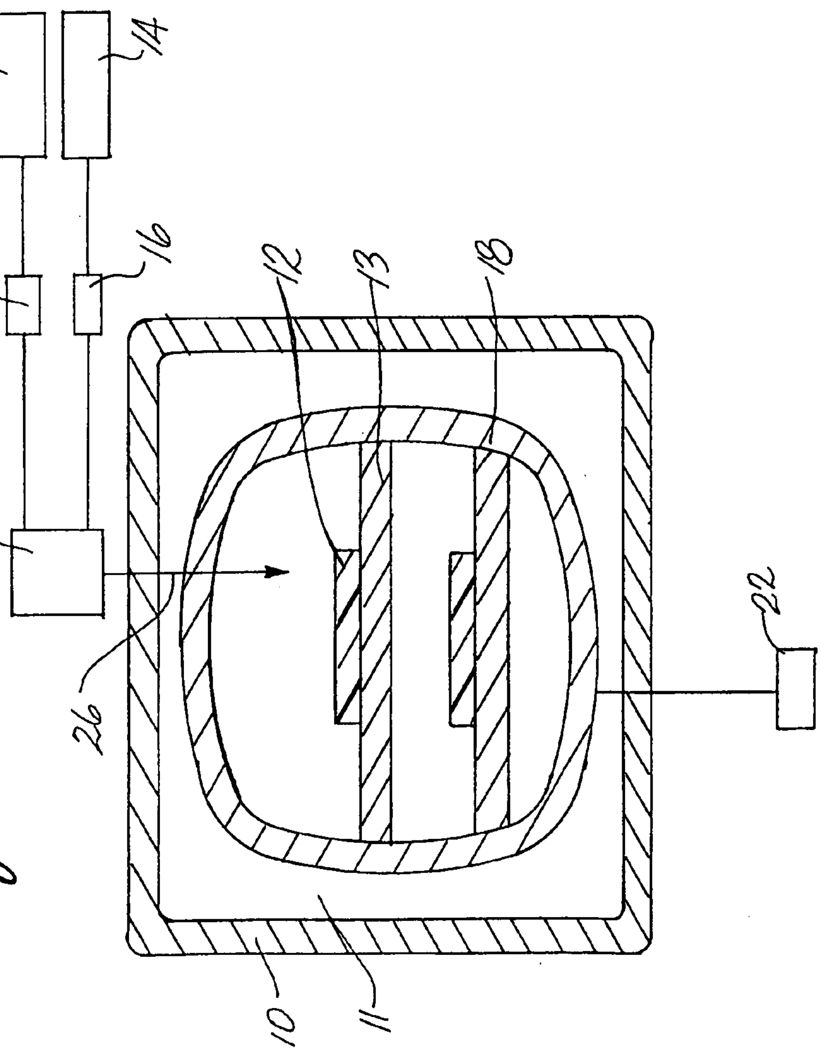


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/15346

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 25/00, 27/00, 31/00, 33/00; A43B 13/04
US CL :156/245, 272.6; 36/30R; 264/483, 259; 428/494, 515
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/245, 272.2, 272.6, 275.7; 36/19.5, 30R, 44; 264/483, 259; 428/317.1, 317.7, 319.3, 494, 515; 427/535, 536, 539

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,820,580 A (HOCKER et al) 11 April 1989 (11-04-89), Abstract, col. 3, lines 1-56.	1, 3-6, 10-13, 22-26, 28, 41, 42, 44-46 ----- 2, 7-9, 14-21, 27, 29-40, 43, 47
Y	US 4,128,950 A (BOWERMAN et al) 12 December 1978 (12-12-78), Abstract, col. 5, lines 14-20.	2, 7-9, 43, 47
Y	US 4,870,129 A (HENNING et al) 26 September 1989 (26-09-89), Abstract, col. 8, lines 1-15.	2, 7-9, 43, 47
Y	US 4,267,202 A (NAKAYAMA et al) 12 May 1981 (12-05-81), Abstract, col. 3, lines 9-40, col. 4, lines 20-25, lines 49-59.	27, 47

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
12 AUGUST 1999	31 AUG 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/15346

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,466,424 A (KUSANO et al) 14 November 1995 (14-11-95), col. 4, lines 2-45.	